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# Cyclic charge–discharge behaviour of sintered plate cadmium electrodes in the presence of organic additives

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The effect of some organic additives on the capacity performance of sintered plate cadmium electrodes has been studied. The additives under investigation were 1,2,3-benzotriazole (BTA), imidazole (IDA) and polyvinyl alcohol (PVA). It has been observed that these compounds minimize the capacity fall during the early cycles. IR spectra results indicate that cadmium (II) is complexed with azole compounds and SEM photographs supplement the results.

## 1. Introduction

The cadmium electrode is of high technological importance as the negative electrode in nickel–cadmium and silver–cadmium alkaline secondary battery systems. There are several significant processes in the electrode performance and degradation such as build-up of cadmium hydroxide crystals which results in recrystallization and redistribution of active material, which affects the discharge and recharge efficiencies. Cadmium can be reversibly charged and discharged via the reaction formally written as

$$\mathrm{Cd} + 2\mathrm{OH}^- \rightleftharpoons \mathrm{Cd(OH)_2} + 2e^-$$

The charge–discharge behaviour of sintered plate cadmium electrodes has been studied previously [1, 2]. The conclusions drawn were that in early cycle life the cadmium crystallites increase in size concurrent with a redistribution of material within the sinter matrix. The early drastic loss in available capacity, although interrelated to both charge and discharge processes, reflected more the inefficiencies of discharge. This is contrary to the findings of Will and Hess [3]. In early cycles they detected large (1–2 $\mu$m) $\mathrm{Cd(OH)_2}$ crystals many of which were observed not to reduce easily on charge.

Recently, the effect of iron addition to the sintered plate cadmium electrode has been studied and it was found that the cadmium electrode containing 20% added iron gave better capacity output at both high and low rates of discharge [4]. The effect of ethyl cellulose [5], and that of carboxy methyl cellulose [6], on cadmium electrodes have also been recommended. More recently organic additives such as PVA, terephthalic acid, cellacol and azole compounds have received attention regarding improvement of the performance of the cadmium electrode.

Such additives are beneficial if they reduce the size of the crystals formed, thereby providing a larger area for the reaction.

It is the objective of the present work to report such a solution. The additives under investigation were 1,2,3-benzotriazole (BTA), imidazole (IDA) and polyvinyl alcohol (PVA). Azole compounds are chemisorbed on the surface of copper to form a protective film which inhibits corrosion [7–9].

## 2. Experimental details

### 2.1. *Cell setup and solution preparation*

The experimental cell comprised one negative plate and two positive plates for a study of the characteristics of the negative plate, so that the plate under investigation limits the capacity. The plates were prepared by sintering carbonyl nickel powder (Type 255) in an inert atmosphere on a punched nickel plated mild steel grid of dimensions 7.5 cm × 6 cm. The thickness of the plates was 0.8 + 0.05 mm and the porosity of the sintered plaque prior to forming ranged between 70 and 75%. The impregnating solutions were prepared from AR grade nickel nitrate for the positive and cadmium nitrate for the negative plates. A vacuum impregnation method, which is generally adopted for preparing the plates, was adopted in this investigation.

### 2.2. *Solubility and introduction of additives into the active material*

BTA and IDA are sparingly soluble in water and soluble in alcohol, benzene, toluene, chloroform and DMF. PVA is essentially soluble in hot and cold water and alcohol–water mixtures.

For BTA and IDA the impregnated electrodes (before formation) were dipped in a 2 wt % solution of the chosen additive in a 80:20 toluene:ethanol mix. Depending upon the solubility of PVA they were dipped in to a solution of PVA in 80:20 hot water:ethanol mix (before formation). The electrodes were soaked for 10 min, taken out, dried at 60° C

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and then subjected to formation. A blank was also prepared for comparison. A minimum of three electrodes were subjected to each test.

### 2.3. *Cell assembly and life cycle tests*

The plates were assembled into cells with two positive plates and nylon cloth as separator. 30% (w/v) potassium hydroxide (AR) was used as the electrolyte. Potentials were referred to Hg/HgO/30% KOH. The cells were cycled for three conditioning cycles to arrive at the practical capacity, designated as *C*. The electrodes were charged at the 0.1 *C* rate for 14 h. The charged electrodes were then discharged at five different rates, *viz.*, 0.1 *C*, 0.2 *C*, 1 *C*, 3 *C* and 5 *C*. The negative plate was considered to have discharged when it reached a potential of −0.75 V at low rates and −0.6 V at high rates with respect to the reference electrode.

Life cycle tests were performed at *C*/2 rate charge and discharge at ambient temperature (30 ± 5° C) to a 80% depth of discharge in each cycle.

### 2.4. *Analysis of the impregnated active material*

An infrared spectrometer was used to see the nature of absorption bands and scanning electron microscopy (SEM) was used to know the crystal structure.

## 3. Results and discussion

### 3.1. *Capacity tests*

The per cent capacity output of the negative plate at different rates is shown in Table 1. At low rates of discharge *viz.*, 0.1 *C* and 0.2 *C*, the capacity is increased in all the treated electrodes whereas the electrode containing only cadmium hydroxide shows the lowest capacity. The capacity output of the plates dipped in BTA passes through a maximum at both low and high rates of discharge. A stabilized capacity output of 67% is obtained for IDA treated electrodes at three different rates (Table 1). It follows from single electrode potential studies that the ohmic drop caused by the adsorbed layers of organic compounds on $Cd(OH)_2$ crystals is 10–15 mV at the *C*/2 rate discharge. The maximum value of 13 mV is obtained with BTA treated electrodes which show the best capacity performance. The ohmic drops caused by the layers of IDA and PVA on $Cd(OH)_2$ crystals are 11 mV and 10 mV, respectively.

*Table 1. Output capacity of cadmium electrodes with and without additive at different rates*

| *Additive* | *Capacity output** (% *at different rates*) | | | | |
|---|---|---|---|---|---|
| | *0.1C* | *0.2C* | *1C* | *3C* | *5C* |
| Blank | 52 | 52 | 50 | 49 | 47 |
| BTA | 72 | 71 | 70 | 70 | 69 |
| IDA | 67 | 67 | 67 | 66 | 64 |
| PVA | 62 | 60 | 59 | 59 | 58 |

* Assuming 100% efficiency.

### 3.2. *Life cycle tests*

The faradaic efficiency of cadmium electrodes with and without additive is shown in Fig. 1. It follows that BTA treated Cd electrodes (B) show a better stabilized capacity utilization of 70% of the theoretical value whereas IDA and PVA treated electrodes (C and D) give capacity utilization of 63% and 58%, respectively. The electrodes prepared in this work without any additive show capacity utilization of 40% of the theoretical value (A) after 20 cycles.

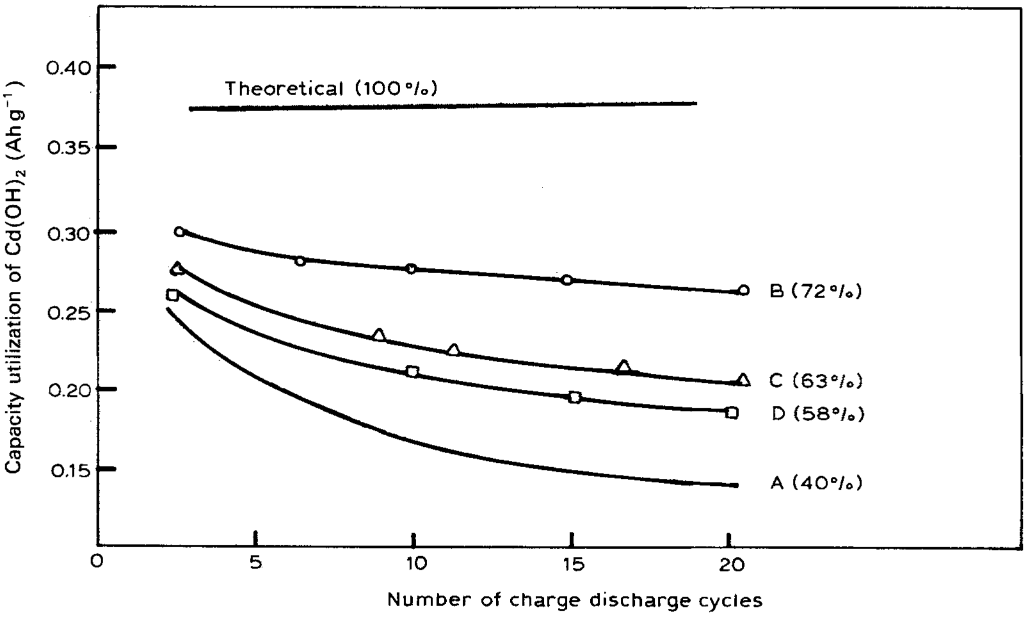


Fig. 1. Capacity utilization of active material (Ah g$^{-1}$) against number of charge/discharge cycles for the *C*/2 rate. DOD: 80%. (A) blank, (B) BTA, (C) IDA and (D) PVA.

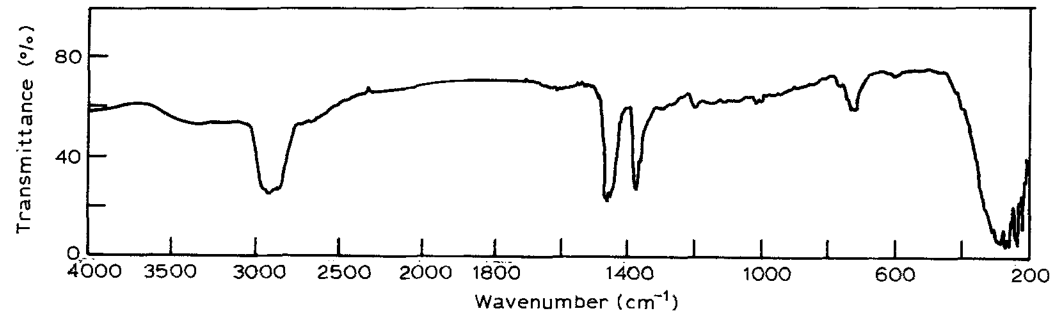


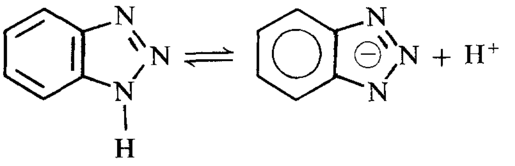
Fig. 2. IR spectra of benzotriazole (BTA).

The purpose of this paper is to note the effect of the above mentioned additives on the capacity of sintered plate cadmium electrodes. It has been observed that these additives minimize the capacity fall during the early cycles. The increase in capacity utilization of organic compound-treated cadmium electrodes may be attributed to the reduction in the size of the crystals formed, thereby leading to large electrochemically-active surface areas for reaction.

### 3.3. *IR spectra*

Figure 2 is the infrared spectrum of BTA which indicates the N–H stretching absorption frequency in the region 3400–2200 $\mathrm{cm}^{-1}$. BTA contains three nitrogen atoms: two are the so-called pyridine nitrogens, the other is a pyrrole nitrogen. In the solid state, the imino group of BTA forms different kinds of hydrogen bonding, N–H . . . N, with the pyridine nitrogen, which shows strong multiple absorption in the region 3300–2300 $\mathrm{cm}^{-1}$. The infrared spectrum of the electroactive material (Cd + BTA) is seen in Fig. 3. It clearly shows the complete absence of the N–H stretching absorption frequency in the region 3400–2200 $\mathrm{cm}^{-1}$ and the N–H bending absorption in the region 1500–1250 $\mathrm{cm}^{-1}$ which indicates the deprotonation of the chemisorbed BTAH. Therefore it is suggested that BTA is present in the form of the deprotonated anion BTA.

In aqueous solution, part of BTA is deprotonated to form $\mathrm{BTA}^-$.



We propose that BTA forms a ligand to the cadmium atom to form a Cd(0)BTA complex; this is then oxidized and deprotonated to form bis(benzotriazolato) cadmium (II).

$$\mathrm{BTAH} + \mathrm{Cd(0)} \longrightarrow \mathrm{Cd(0)BTA} \xrightarrow{O_2} \mathrm{Cd}^{2+}(\mathrm{BTA})_2^-$$

In fact, it has been reported in the literature that imidazolato-metal (I) is a polymeric material [10]. Reference has been made to X-ray crystallographic evidence which indicates that bis(imidazolato) zinc is polymeric [11]. Therefore it is suggested that the polymer film covering the surface of the cadmium electrode enhances the electrochemically-active surface areas.

### 3.4. *SEM analysis*

Figures 4 to 7 are scanning electron micrographs (× 300) of the middle section of the electrodes (Blank, BTA, IDA and PVA), previously cycled at the *C*/2 charge, *C*/2 discharge rates, removed in the discharged state after 20 cycles. There is an increase in the crystal size of the hexagonal $\beta$-$\mathrm{Cd(OH)_2}$ crystals (Fig. 4, Blank). Armstrong *et al.* [12] prefer the direct formation of a passivating film on the surface of the active material during discharge as the cause of the premature failure of the negative electrode.

Complex formation is clearly visible in Figs 5 and 6 which give at the same time the best capacity performance and a large number of smaller $\mathrm{Cd(OH)_2}$ crystals is clearly seen in Fig. 4. Figures 5 to 9 are SEM photographs of the middle section of the electrodes (Blank, BTA, IDA and PVA), previously cycled at the *C*/2 charge, *C*/2 discharge rates, removed in the charged state after 20 cycles. Earlier investigators [13–15] found that cadmium crystals can increase in size-

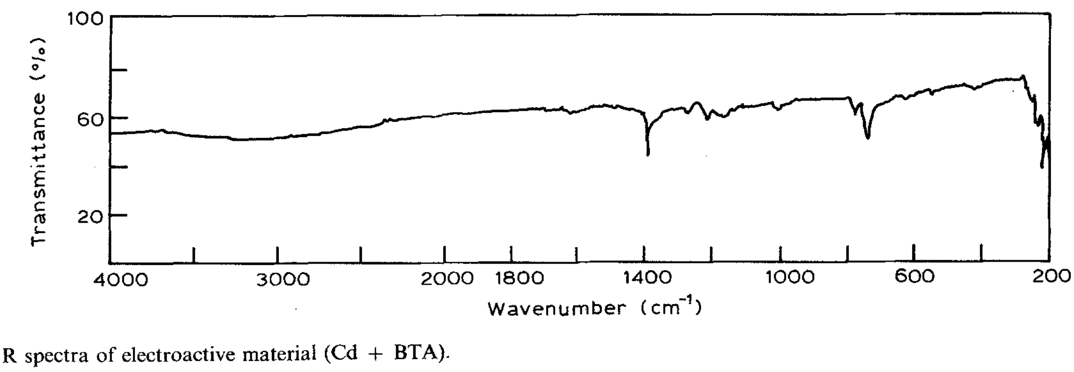


Fig. 3. IR spectra of electroactive material (Cd + BTA).

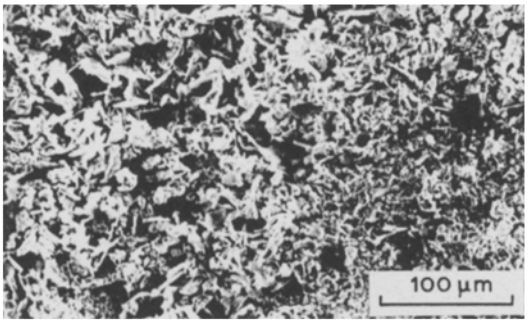


Fig. 4. Central area of an electrode (Blank) in the discharged state after 20 cycles at the *C*/2 charge, *C*/2 discharge rates (× 300).

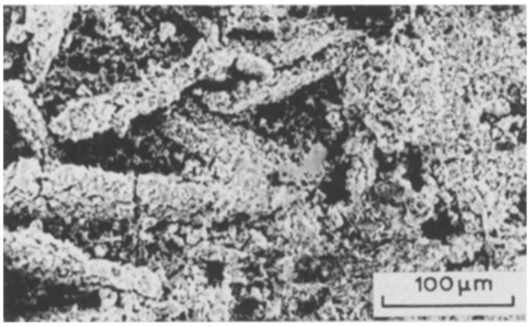


Fig. 5. Central area of an electrode (BTA), conditions are the same for Fig. 4 (× 300).

considerably during cycling and, once formed, are not easily recharged. This is clearly seen in Fig. 8. It is apparent from Fig. 8 that as cycling proceeds charging of the $Cd(OH)_2$ is also becoming less efficient. This may be related to an increase in the crystal size of the hexagonal $\beta$-$Cd(OH)_2$. The uniform distribution of active material is shown in Fig. 12.

## 4. Conclusion

The organic additives studied minimize the capacity fall during the early cycles. The increase in capacity utilization of organic compound treated cadmium electrodes is attributed to the reduction in the size of the crystals formed, thereby leading to large electrochemically active surface areas for reaction.

The main findings can be summarized as follows:

(i) life cycle tests show that the faradaic efficiency is the maximum in the case of BTA-treated cadmium electrode;

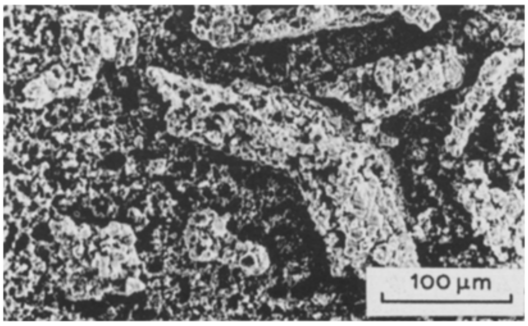


Fig. 6. Central area of an electrode (IDA), conditions are the same for Fig. 4 (× 300).

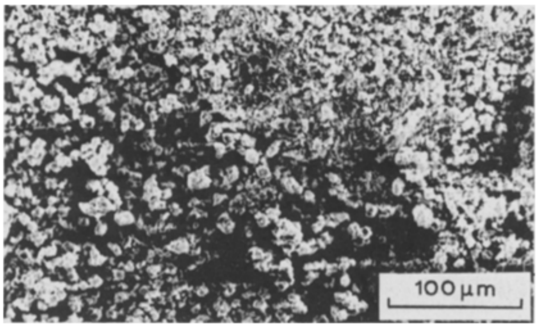


Fig. 7. Central area of an electrode (PVA), conditions are the same for Fig. 4 (× 300).

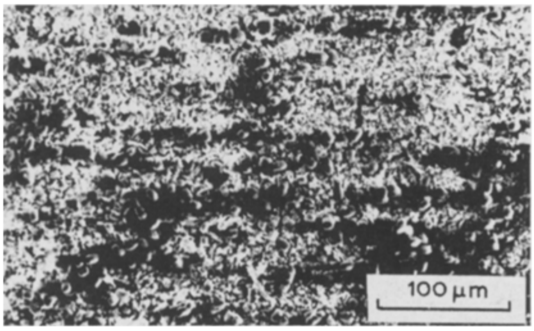


Fig. 8. As Fig. 4 but electrode in charged condition (× 300).

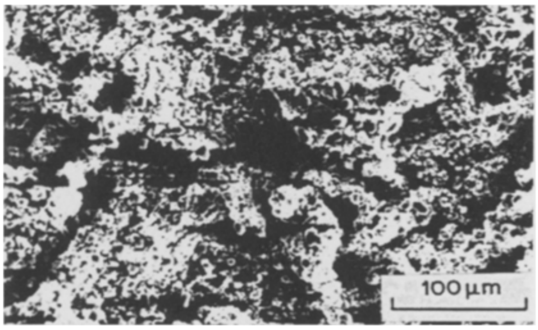


Fig. 9. Central area of an electrode (BTA), conditions are the same for Fig. 8 (× 300).

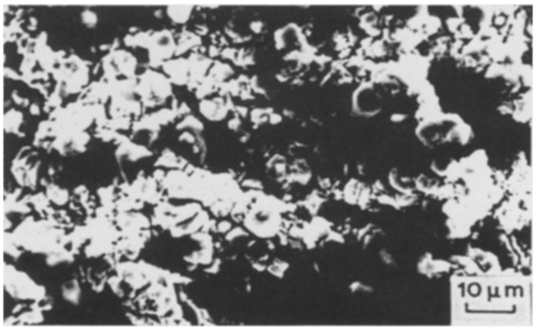


Fig. 10. As Fig. 7 but at higher magnification (× 1000).

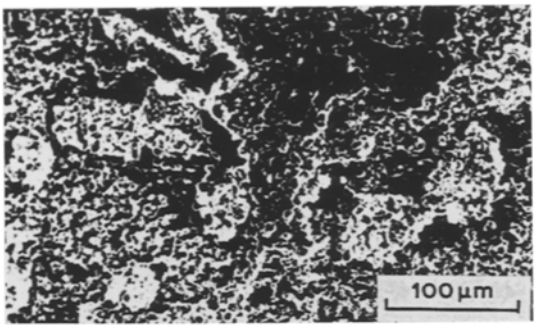


Fig. 11. Central area of an electrode (IDA), conditions are the same for Fig. 8 ( × 300).

(ii) IR spectra studies indicate that bis(benzotriazolato) Cd(II) is formed; and

(iii) SEM analysis demonstrates complex formation; BTA and IDA form complexes with cadmium which give better capacity output whereas the increase in capacity utilization of PVA-treated cadmium electrodes is attributed to the reduction in the size of the crystals formed, thereby leading to large electrochemically active surface areas for reaction.

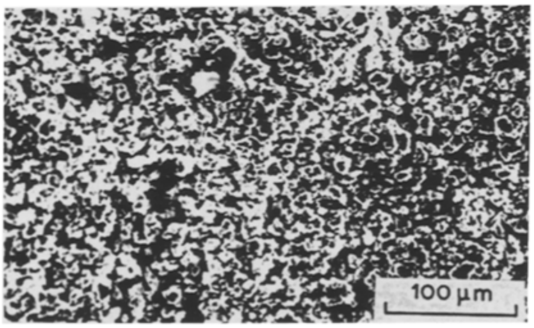


Fig. 12. Central area of an electrode (PVA), conditions are the same for Fig. 8 ( × 300).

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## References

[1] R. Barnard, J. A. Lee, A. H. Rafinski and F. L. Tye, 'Power Sources', Vol. 5, edited by D. H. Collins, Academic Press, London (1975) pp. 183–209.

[2] R. Barnard, K. Edmondson, J. A. Lee and F. L. Tye, *J. Appl. Electrochem.* **6** (1976) 107.

[3] F. G. Will and H. J. Hess, *J. Electrochem. Soc.* **120** (1973) 1.

[4] S. Tamil Selvan, S. Nathira Begum, VR. Chidambaram, R. Sabapathi and K. I. Vasu, *J. Power Sources* **32** (1990) 55.

[5] S. Sathyanarayana, *J. Appl. Electrochem.* **15** (1985) 453.

[6] S. Tamil Selvan, R. Sabapathi and N. Venkatakrishnan, *Bull. Electrochem.* **6** (1990) 266.

[7] G. W. Poling, *Corros. Sci.* **10** (1970) 359.

[8] C. McCrory-Joy and J. M. Rosamilia, *J. Electroanal. Chem.* **136** (1982) 105.

[9] Gi Xue, Jianfu Ding, Peiyi Wu and Gending Ji, *ibid.* **270** (1989) 163.

[10] G. P. Brown and S. A. Aftergut, *J. Polym. Sci., Part A* **2** (1964) 1839.

[11] M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.* **84** (1962) 1543.

[12] R. D. Armstrong, A. D. Sperrin, F. L. Tye and G. D. West, *J. Appl. Electrochem.* **2** (1979) 265.

[13] Y. Okinaka and C. M. Whitehurst, *ibid.* **117** (1970) 583.

[14] G. W. Bodamer and A. J. Salkind, in 'Batteries', edited by D. H. Collins, Proc. 4th Int. Power Source Symp., Pergamon, London **2** (1964) 55.

[15] E. Luksha and D. J. Gordy, NASA Report CR-122 (1971) 371.